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REMOVAL OF ORGANIC CONTAMINANTS FROM AIR BY TYPE 13X MOLECULAR SIEVE

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ABSTRACT

The adsorption of low concentrations of n-decane, methane, benzene, toluene, xylene, pyridine, aniline, and nitrobenzene on type 13X Linde molecular sieve has been studied at influent concentrations of from 5 to over 100 ppm and superficial linear velocities (velocities if no sieve were present to reduce the cross section) of up to 3000 cm/minute. The breakthrough weight capacity at a flow rate of 2500 cm/minute for a representative aliphatic compound (n-decane) was 10 wt-% of the sieve and for a mononuclear aromatic (benzene) was 0.35 wt-% at 25°C. Decreasing the flow rate of the aromatic to 500 cm/minute increased the breakthrough capacity to 2.1%.

Regeneration conditions were also studied. Water vapor readily displaces organic adsorbates (except high boiling polar compounds) at room temperature. Therefore, molecular sieve with coadsorbed water may be reactivated by passing dry air at 200° to 325°C in the same direction of gas flow as that used during the adsorption cycle. The coadsorbed water will displace the sorbed organic compounds as it moves down the column, whereas the organic materials would be pyrolyzed in place if the water were not there.

PROBLEM STATUS

This is a final report on this phase; work is continuing on other phases of the problem.

AUTHORIZATION

NRL Problem C08-05
BuShips Project SF 013-08-03

REMOVAL OF ORGANIC CONTAMINANTS FROM AIR
BY TYPE 13X MOLECULAR SIEVE

INTRODUCTION

In studying a possible regenerative system for controlling the carbon dioxide level in submarine atmospheres, it was also desirable to investigate the ability of such a system to reduce the concentration of organic contaminants. Therefore the following compounds were studied with regard to their adsorption and desorption on type 13X Linde molecular sieve: methane, n-decane, benzene, toluene, xylene, pyridine, aniline, and nitrobenzene.

Type 13X molecular sieve is a synthetic sodium zeolite with a crystal structure consisting (after removal of water) of mutually connecting intracrystalline voids which are uniform in size and amount to some 51 vol-% of the zeolite. This particular type of sieve will admit molecules with critical diameters up to 13 angstroms. The internal surface area is 700 to 800 square meters per gram and external surface area 1 to 3 square meters.

In this study the following parameters were investigated:

1. Organic vapor concentration was varied from 3 ppm to 10% (all gas concentrations are by volume unless otherwise stated).

2. Superficial linear velocity (the velocity if no sieve were present to reduce the cross section) ranged from 500 to 4000 cm/minute (all velocity figures are superficial unless otherwise stated).

3. Relative humidity ranged from 0 to 100%.

4. Gas temperatures were varied from 20° to 30°C.

Regeneration conditions tried were (a) heat alone, (b) heat plus a purge gas of N_2, air, or CO_2, and (c) replacement of the organic compounds by H_2O followed by desorption of H_2O. In addition replacement of sorbed CO_2 by organic vapors was studied.

EXPERIMENTAL PROCEDURE

Adsorption

The apparatus used for these measurements is shown schematically in Fig. 1. It can be divided into three functional sections: (a) purification and flow regulation of the carrier gas stream; (b) introduction and homogeneous mixing of the organic vapor at a known concentration; (c) measurement of adsorption of the organic vapor by a determination of the residual concentration in the effluent gas. The compressed air line was fitted with a filter to remove any oil or particulate contamination and a regulator-reducer to reduce the pressure from 100 to 12 psi. No pressure variation was noticeable on a manometer calibrated in mm Hg. The flow of this regulated air was controlled by a fine needle valve.
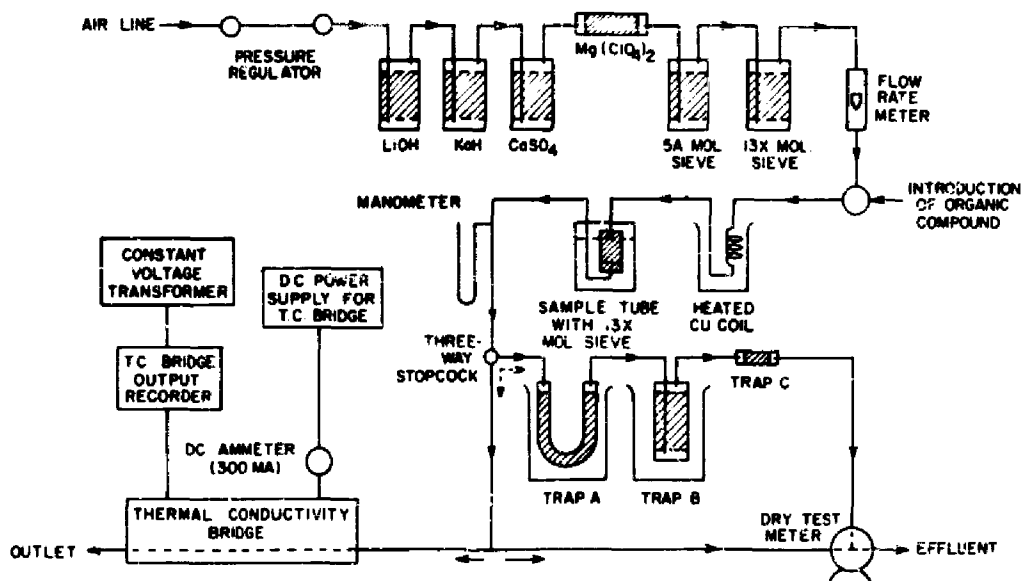
Fig. 1 - Molecular sieve adsorption apparatus

The following chemicals were employed in purification of the carrier gas. For removal of CO_2:

1. Lithium hydroxide filled a 2-liter suction flask; the exit end contained 10 grams of indicating soda lime.

2. Two hundred grams of potassium hydroxide pellets were placed in a drying jar (overall height 300 mm).

For removal of H_2O:

1. Indicating Drierite was used in two drying towers and one 500-ml suction flask.

2. Magnesium perchlorate was placed in a drying tube (length 150 mm).

3. Type 5A Linde molecular sieve (1/16-inch pellets) filled a 1000-ml suction flask.

Organic contaminants were removed on type 13X molecular sieve (1/16-inch pellets) in a drying jar.

Fifteen-gram 13X molecular sieve blanks in the sample container showed no increase in weight in 64 hours (17,500 liters of air at 20°C). These blanks were run every weekend unless an adsorption experiment was in progress.

The organic compound was introduced into the gas stream by three methods:

Method 1 was for organic vapor concentrations up to 10%. The organic compound was fed from a 10-ml burette with 0.05-ml divisions spaced 4 mm apart. Uniform mixing was assured by passing the organic vapor-air mixture through a 20-foot copper coil, of 1/8 inch inside diameter, heated to 200°C in a silicone oil bath.

Method 2 was for organic vapor concentrations of 50 to 200 ppm; the organic compound was placed in a 50-ml suction flask, stoppered with a two-hole neoprene stopper. Inserted in the stopper were a 1/4-inch glass connector tube bent at a right angle and a thermometer with a range of +50 to -50°C. The concentration of organic vapor picked up by the carrier gas, which entered the flask through the side arm, was controlled by placing the flask in a dry ice-ethanol slush and maintaining the temperature in the flask constant. This was accomplished by adjustment of the level of the dry ice slush. For example, with benzene in the flask at -76.8°C and the air stream temperature in the flask at -28°C, the benzene dew point downstream was -57°C (180 ppm); with the air temperature inside the flask at -32°C the dew point was -60.5°C (135 ppm). Close agreement (within 1/2%) was obtained between the amount of organic vapor available to the sieve calculated from the influent concentration using the Antoine vapor pressure equation (1) at the measured dew point, and the amount actually adsorbed on the molecular sieve (determined by weight change).

Method 3 was for organic concentration of 1 to 20 ppm. The side arm of the same 50-ml suction flask was sealed shut, and the right-angled glass connector was replaced by a T-shaped connecting tube. The carrier gas flowed through the horizontal arms of the T-connector. The opening of the inserted vertical arm was varied from 0.1 mm to 3 mm in diameter, depending upon the organic vapor concentration desired and the volatility. On removal of this flask from the adsorption train, the horizontal arms of the T-connector could be sealed with rubber policemen and the assembly weighed on an analytical balance. This method gave constant influent concentrations of organic vapor for long periods when the flask was thermostated. The system was operated at 25° and 30°C, thus doing away with the necessity of a dry ice bath.

The sample tube dimensions were 1.52 cm in inside diameter and 16 cm in length. When filled to a bed depth of 12 cm with activated type 13X molecular sieve, the tube contained about 12 grams of material. This sample tube was immersed in a constant temperature bath.

The lot from which molecular sieve samples were obtained was periodically checked for vestigial contamination by purging with dry N_2 at 300°C and measuring the weight change. It was found that atmospheric gases, particularly nitrogen (2), would be adsorbed to equilibrium in a matter of minutes at room temperature and atmospheric pressure, the weight gain being nearly 1%.

A thermal conductivity cell analyzer (3) was used for the measurement of organic concentrations above 25 ppm in the effluent gas stream. Three hundred ml/minute of the effluent gas were passed through the thermal conductivity cell at its operating temperature of about 43°C. The remaining effluent gas bypassed the detection system and flowed through a dry test meter into the room. Fifty grams of 13X molecular sieve were used as the organic vapor adsorbent between the sample cells and the reference cells of the thermal conductivity bridge. Since the cells were wired in a Wheatstone bridge circuit, any difference between the rates of heat loss from the sample and reference filaments would cause the bridge to become unbalanced to an extent proportional to the difference in composition between the sample and reference gas — in this case the organic vapor concentration.

For measurements of organic concentrations below 25 ppm a modified method of Quiram, Metro, and Lewis (4) involving the use of traps containing silica gel at -76°C was used in place of the thermal-conductivity-bridge system. Type 13X molecular sieve replaced silica gel because the gas flow could not be maintained constant through the gel. Activated charcoal at -78°C also gave variable flows. Another consideration, in addition to maintaing a constant gas flow, was the degree of attraction between adsorbate and

adsorbent molecules. Molecular sieves are capable of adsorbing both polar and nonpolar organic compounds more strongly than activated silica gel (5). For example, at 25°C and a partial pressure of 10 mm Hg, propane (a nonpolar aliphatic) will be adsorbed on type 5A molecular sieve up to 7.5 wt-%, while silica gel sorbs only 0.5 wt-%. It is very probable, at the temperature employed (-76°C), that molecules with critical diameters larger than 13A will either condense on the external surface of the sieve or on the walls of the trap. In employing this method the procedure was as follows: About 25 grams of molecular sieve were placed in a glass-stoppered U-tube (1.5-cm inside diameter and 24 cm long). Dow Corning high-vacuum grease was used to ensure airtight seals. Later rubber stoppers were used in place of glass and no weight gain was noticed on standing 24 hours at room or dry ice temperatures for either the glass-stoppered or the rubber-stoppered tube. During an adsorption experiment three of these tubes (marked traps A, B, and C) were used. Traps A and B were placed in a dry ice-ethanol bath. Any organic vapor in the effluent from the molecular sieve sample tube was adsorbed (or condensed) in trap A; traps B and C protected trap A from outside contamination. After a run was completed, trap A was allowed to reach room temperature gradually, since molecular sieves adsorb relatively large quantities of nitrogen and oxygen at dry ice temperatures (5) and the rapid evolution of these gasses on warming might displace the adsorbed organic compounds.

It was found that 13X molecular sieve at 30°C would adsorb quantitatively a wide range of organic vapor concentrations to a sieve loading of up to 1/3 wt-% at a gas velocity of 3000 cm/minute, for all the organic compounds tested except methane. This eliminated the need for dry ice cooling except as an initial check on the retention of each new organic compound on the 13X molecular sieve. Therefore, traps A and B were not cooled to -76°C, and it was possible to maintain a constant weight check on them.

The organic concentration of the effluent from the sample tube was calculated, for small weight increments, by the following formula:

$$\text{effluent conc. (ppm)} = \frac{\text{mg trapped in A}}{\text{mg influent}} \times \text{influent conc. (ppm)}.$$

Since the effluent concentration was continually increasing after breakthrough, the calculated effluent concentration was really an average for that interval, but for small increments of adsorption it represents the true effluent concentration at the midpoint of this adsorption interval. Thus the weight-percent sorbed in the sample at a given time interval was calculated in the following manner:

$$\text{wt-\% sorbed} = \frac{\left(\begin{array}{c}\text{wt of available}\\\text{organic vapor}\end{array}\right) - \left(\begin{array}{c}\text{wt gain of}\\\text{trap A}\end{array}\right)}{\text{initial wt of sieve sample}} \times 100.$$

The amount of adsorbate available to the sample was determined by three methods:

1. From the sum of the weights gained in the sample tube and trap.

2. From the loss in weight of the T-tube-Erlenmeyer flask assembly.

3. By increasing the linear velocity of the carrier gas exactly 20% above the described flow and diverting 1/6 of this new flow through another tube having the same dimensions and weight of 13X molecular sieve (breakthrough capacity 2%). Thus the amount adsorbed in the second tube multiplied by five, equaled the amount available to the sample tube.

The organic vapor influent concentration was calculated as follows:

$$ppm = \left(\frac{mg\ available}{1000\ liters\ gas}\right)\left(\frac{22.41}{mol\ wt}\right)\frac{(760)}{(273)}\frac{(gas\ temp.\ in\ °K)}{(baro.\ press.\ in\ mm\ Hg)}.$$

Reactivation

Reactivation studies on molecular sieves by heat, nitrogen purging, and water displacement were performed on 50-gram samples with bed length 12 cm and bed diameter 2.5 cm, or on 12-gram samples with bed length 12 cm and bed diameter 1.5 cm. The samples were heated in an oven with a purge of dry nitrogen (dew point below -76°C) at a gas velocity of 100 cm/minute. For studies on the displacement of organic vapors by H_2O at room temperatures, the thermal conductivity apparatus was used in determining the rate of organic compound displacement and the H_2O breakthrough time.

A closed system regeneration apparatus was also set up. A 2-liter volume of air was circulated at a velocity of 100 cm/minute through a 50-gram bed of 13X molecular sieve, containing 4 wt-% n-decane and 5 wt-% H_2O. For measurement of temperature a chromel-alumel thermocouple was placed in contact with the sieve. Heating was by a Variac-controlled nichrome wire heater wound on the surface of the sample tube. The temperature was increased at a rate of 11°C/minute for 25 minutes and then was held at 300°C for 15 minutes. During the heating cycle the evolved water and organic vapors were frozen out in a cold trap at -72°C. The sieve was then sealed from the air in the system, and the bed allowed to cool to room temperature. The regeneration was complete and charring did not occur. However, charring did occur with a sample containing 4 wt-% n-decane without coadsorbed water. The regenerated H_2O n-decane sample later adsorbed 28% of its net weight at equilibrium with 25°C, 50%-relative-humidity air, indicating that the closed system regeneration procedure did not decrease its capacity to absorb water.

EXPERIMENTAL RESULTS

Isothermal Adsorption

Normal decane (Phillips 66, 99 mol-% minimum) was the first organic compound investigated (Figs. 2-5). Over a wide range of concentrations, increasing the flow rate from 500 cm/minute to 5000 cm/minute reduced the breakthrough capacity, as measured by the thermal conductivity apparatus, only 1-1/2 wt-% and the equilibrium capacity only half of that (Fig. 2). This corresponds to contact times of 1.14 seconds to 0.114 second. It indicates that the n-decane molecule experiences little difficulty in penetrating the pores of the sieve. One would expect this from the large difference between their diameters, the pore being 13A and n-decane 4.89A (6). Also since this compound has a relatively high boiling point (174°C), the equilibrium weight capacity is higher than it would be for a lower boiling nonpolar aliphatic.

With all factors constant except linear velocity, the required time for breakthrough per unit length of sieve was found (Fig. 4) inversely proportional to the linear velocity over a wide range of flows for compounds that meet the following conditions: (a) the critical diameter must be small relative to pore size, and (b) if nonpolar, the compound must have a vapor pressure comparable to water or lower. Molecules having diameters nearly that of the pore, will require a longer contact time in order to enter the void. Thus, for molecules in this category, doubling the flow rate may shorten the breakthrough time to less than half the original value.
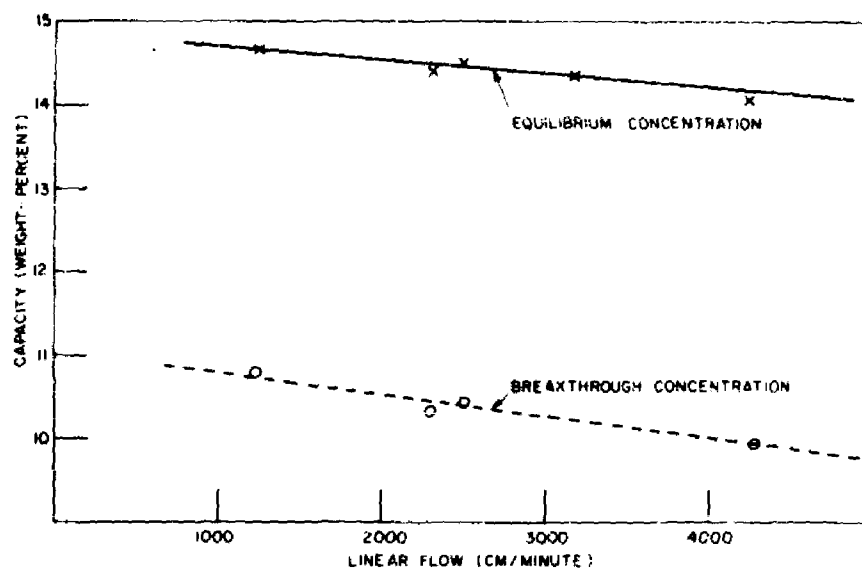
Fig. 2 — Effect of flow rate of 1000-ppm n-decane
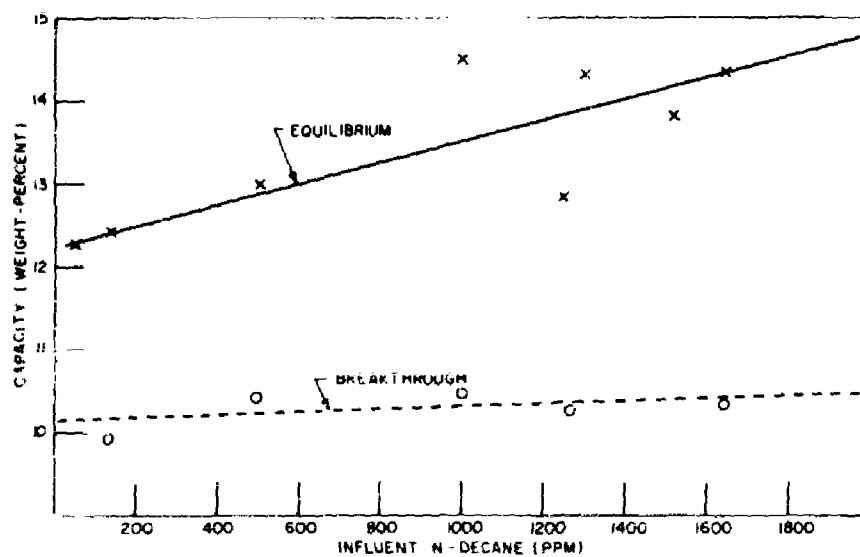at 20°C on the capacity of 13X molecular sieve

Fig. 3 — Effect of concentration of n-decane at 20°C
and a flow rate of 2500 cm/minute on the capacity of
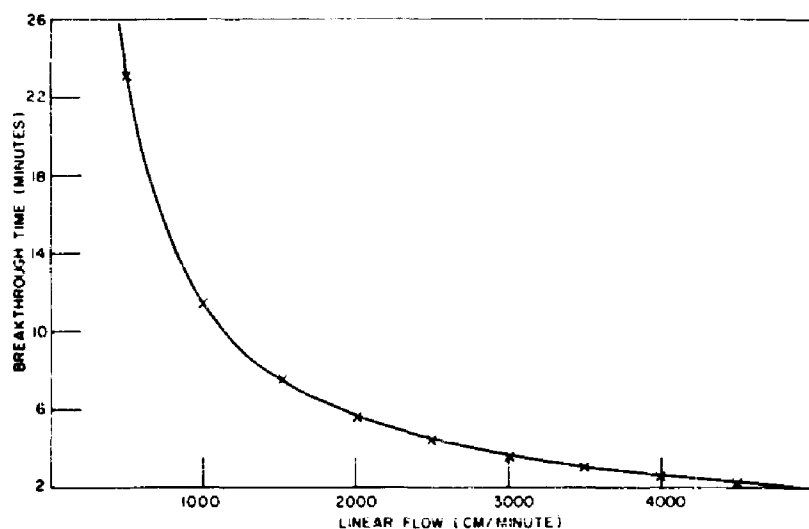13X molecular sieve

Fig. 4 — Effect of flow rate of 1000-ppm n-decane at 20°C on the breakthrough time per centimeter of bed height of 13X molecular sieve
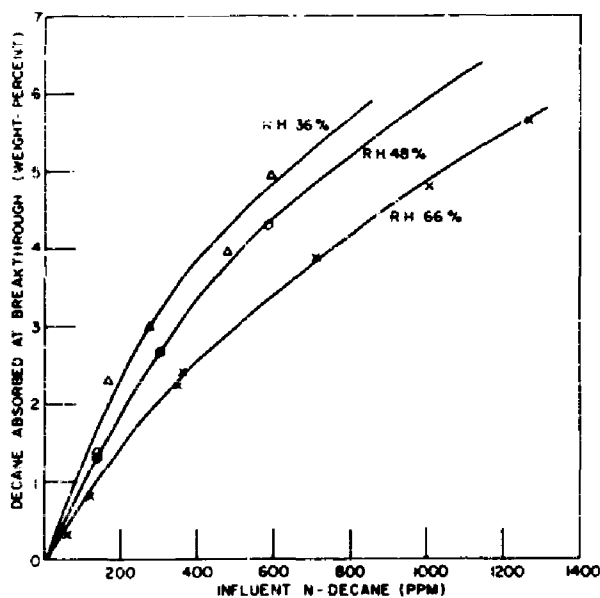

Fig. 5 — Effect of relative humidity on the relationship between the breakthrough capacity of 13X molecular sieve and the breakthrough concentration of n-decane at 20°C and a flow rate of 2500 cm/minute

When coadsorption of n-decane and H_2O takes place on 13X sieve (Fig. 5), the weight-percent of decane sorbed at breakthrough drops sharply below what is sorbed from dry air. For example, at a decane concentration of 100 ppm in air with 48% relative humidity the organic vapor loading drops to 1 wt-% from a value of 10.1 wt-% with dry air; at the same time 13.5 wt-% of water is adsorbed. This is to be expected since the concentration of organic vapor is small relative to that of water. A sixfold increase in the decane concentration (R.H. still 48%) increases the breakthrough capacity to 4.4 wt-%; the weight of water coadsorbed is 10 wt-%.

The above relationship did not hold true for coadsorption of CO_2 and H_2O on molecular sieve. For example, 5A type molecular sieve at 20°C adsorbed 4.4 wt-% CO_2 at break-through from dry air containing 1-1/2% CO_2. At 50% R.H. ($H_2O = 8.76$ mm Hg) 3.3 wt-% CO_2 and 4.38 wt-% H_2O were adsorbed, and at 100% R.H. ($H_2O = 17.53$ mm Hg) 2.2 wt-% CO_2 and 8.76 wt-% H_2O were adsorbed.

In general the adsorption bed is considered to consist of a water adsorption zone and an organic vapor adsorption zone. The water continuously moves the organic vapor adsorption zone ahead of it (5). The amount of sieve available for organic vapor adsorption may be estimated by subtracting the weight of sieve occupied by water from the original weight of sieve material. The weight occupied by H_2O may be roughly defined as:

$$\text{total weight of active sieve} \times \frac{\text{wt-\% } H_2O \text{ sorbed}}{H_2O \text{ breakthrough capacity in wt-\%}} .$$

Then the product of the weight of sieve available for organic vapor adsorption times the organic weight-percent capacity at breakthrough equals the weight of organic vapor capable of being held by the sieve along with the known sorbed water. Since more than one organic vapor impurity will probably be coadsorbed along with water, the compound having the lowest breakthrough capacity should represent the group.

Type 13X sieve will adsorb at room temperature (25 to 35°C) about 2% of its weight of benzene before breakthrough at 5 ppm and a gas velocity of 500 cm/minute (Fig. 6). Increasing the flow to 2500 cm/minute decreases the breakthrough capacity to 0.35 wt-%. The equilibrium capacity at this flow is 4.5 wt-%. The adsorption is isothermal at these low organic vapor concentrations if water is not present.

At 100 ppm, 500 cm/minute, and 25°C the breakthrough capacity for benzene is 7.5% (Fig. 7). Increasing the linear velocity to 2500 cm/minute lowers the capacity to 1.9%. Lowering the influent temperature from 30°C to 20°C does not increase the breakthrough capacity of the sieve by more than 0.2%, but it will increase the equilibrium capacity about 1.5% (Fig. 8).

The molecular sieve capacity for toluene at breakthrough is nearly the same as for benzene. At 25°C, 2500 cm/minute linear velocity, and an influent concentration of 3.5 ppm, the breakthrough capacity is 0.4% (Fig. 9). The equilibrium capacity at 3 ppm is 4.25 wt-%, while for benzene the equilibrium at 3 ppm is 2.8 wt-%.

Aniline because of its higher boiling point (184.4°C) would be expected to be adsorbed on the sieve to a greater extent than benzene (B.P. 80.1°C) and this is borne out experimentally. Under similar conditions (temperature, 25°C, linear flow, 2500 cm/minute, and concentration, 135 ppm) the breakthrough capacity for aniline (Fig. 10) is 4.6 wt-% as compared with benzene's 1.9 wt-%. The equilibrium capacity at 60 ppm is 11.5% whereas for benzene it is 10.8 wt-%.
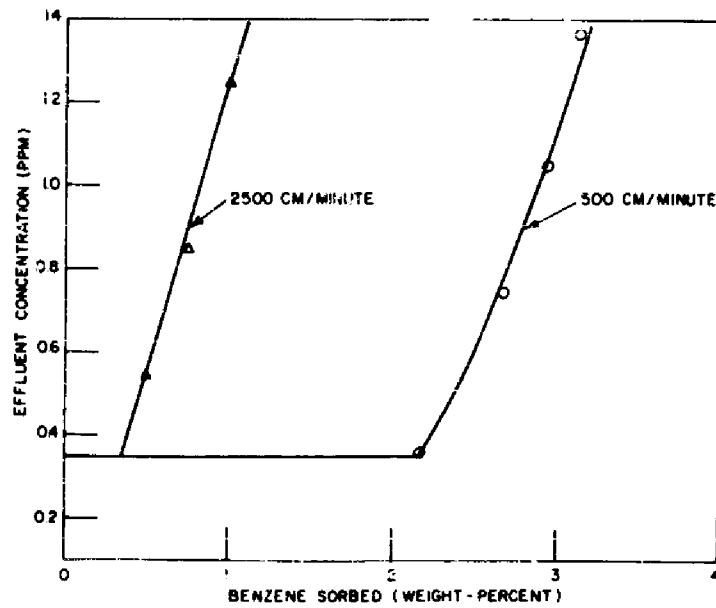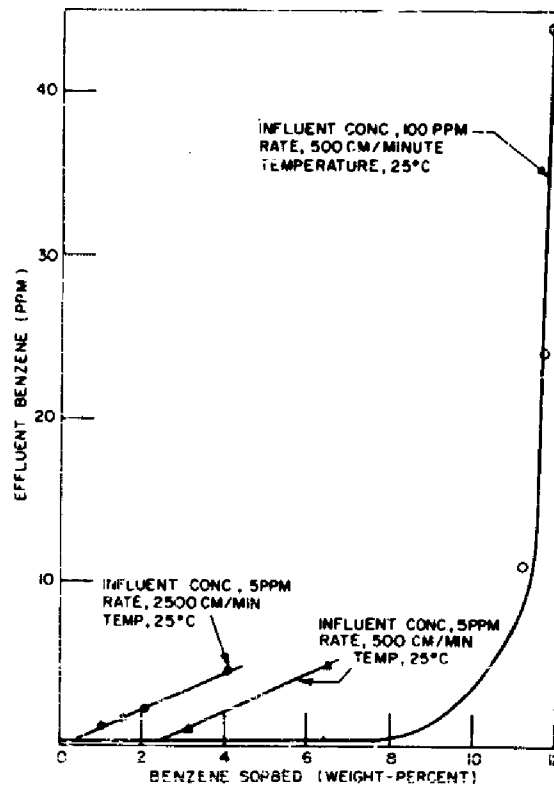
Fig. 6 — Effect of flow rate on the breakthrough
on 5-ppm influent benzene at 25°C

Fig. 7 — Effect of influent benzene
concentration on breakthrough
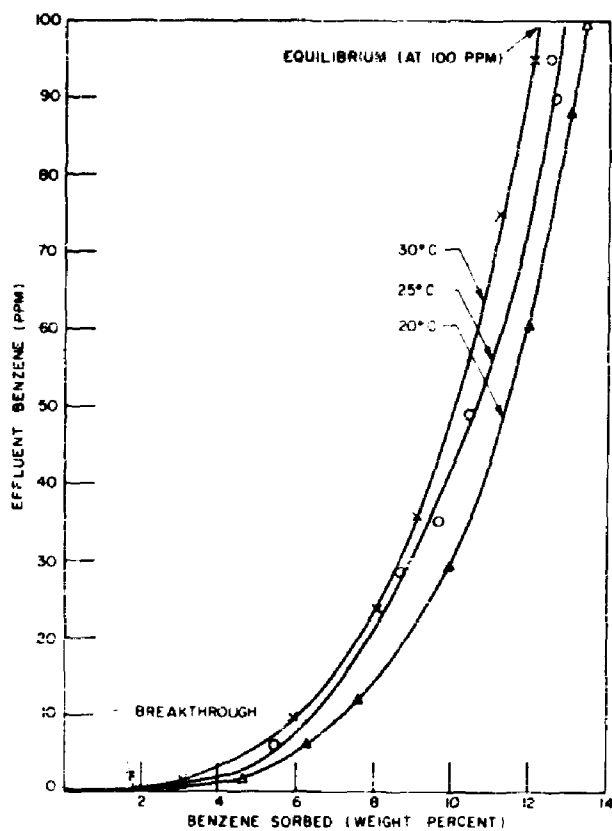
Fig. 8 — Effect of temperature on the breakthrough and equilibrium capacities for 100-ppm benzene at an influent flow rate of 2500 cm/minute
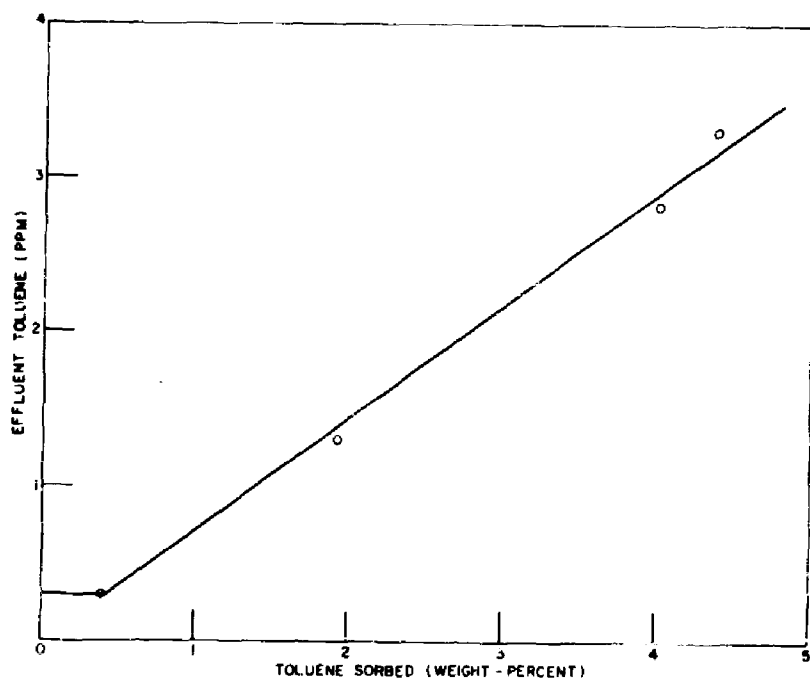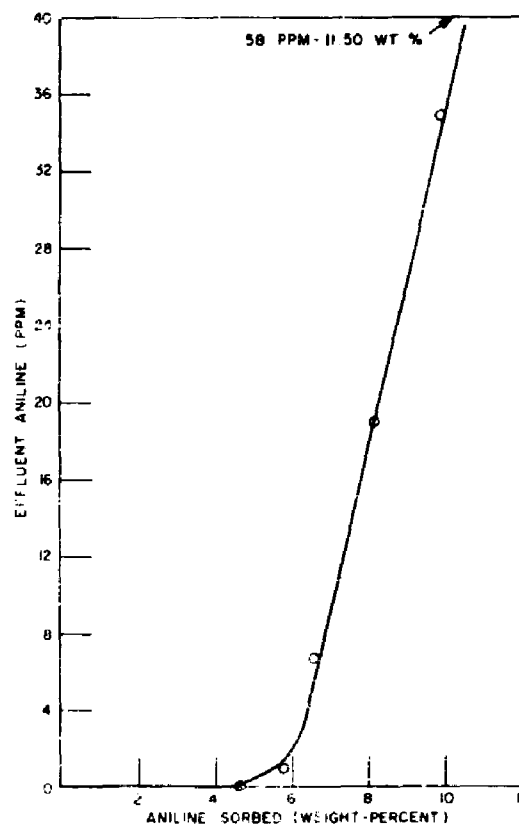

Fig. 9 — Capacity for 3.5-ppm toluene at 25°C and an influent flow rate of 2500 cm/minute

Fig. 10 — Capacity for 135-ppm aniline at 25°C and an influent flow rate of 2500 cm/minute

The aniline dew point at breakthrough was -72°C. Since aniline's boiling point is nearly twice that of water, the -72°C dew point of aniline indicates a concentration probably much less than 2 ppm.

Figure 11 presents data for a low concentration of nitrobenzene, which is a high boiling polar compound similar to aniline.

Table 1 summarizes the breakthrough weight capacities for the aromatic compounds studied.

Under isothermal conditions doubling the path length did not increase the organic compound breakthrough capacity of the sieve material. This did not hold if the adsorption was adiabatic, i.e., with large concentrations of the organic compound and insulation of the sieve bed. In the isothermal case, the gas contact time was doubled by doubling the path length, but the time the gas remained in any single void (if adsorption did not take place) was still unchanged. Aromatic compounds with critical diameters not larger than 10A probably attain equilibrium with the sieve readily, and therefore for such molecules, the effect of critical diameter on the breakthrough capacity should be negligible. (Equilibrium is considered to mean that all the surface area available for that particular influent concentration is filled.)

The adsorbed aromatics are firmly bound to the internal surface of the sieve (7,8). A sieve sample containing 12 wt-% toluene retained all its adsorbate when flushed with purified air for 16 hours at a linear velocity of 3000 cm/minute. The air used for flushing flowed in the same direction as the toluene-containing influent.
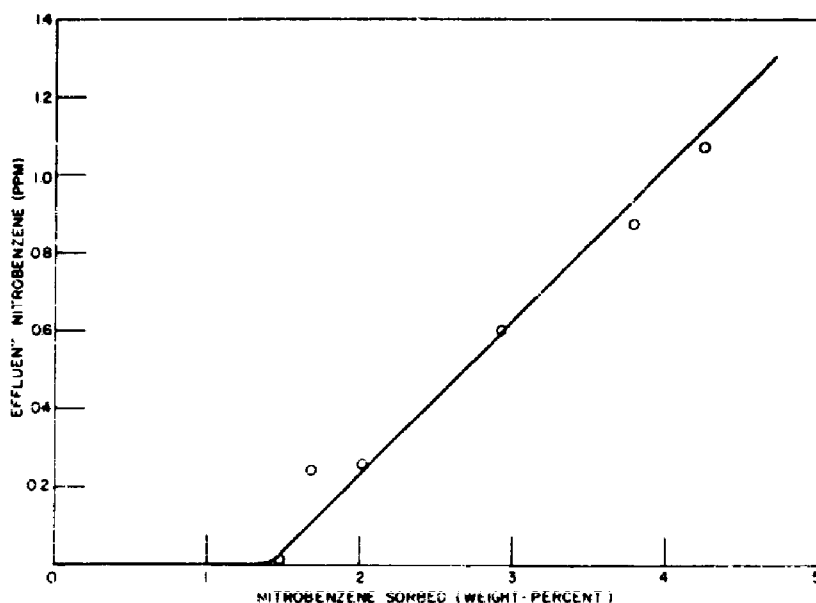
Fig. 11 — Capacity for 15-ppm nitrobenzene at 25°C
and an influent flow rate of 2500 cm/minute

Table 1
Breakthrough Weight Capacities at 25°C
on Type 13X Molecular Sieve

Adsorbate	Influent Conc. (ppm)	Superficial Linear Velocity (cm/minute)	Weight-% Sorbed at Breakthrough
n-Decane	25	2500	10.0
n-Decane	100	2500	10.1
Benzene	5	500	2.12
Benzene	100	500	7.50
Benzene	5	2500	0.35
Benzene	135	2500	1.90
Pyridine	5	2500	0.40
Xylene	5	2500	0.55
Toluene	3.5	500	2.20
Toluene	3.5	2500	0.40
Toluene	100	2500	2.65
Aniline	135	2500	4.70
Nitrobenzene	15	500	2.90
Nitrobenzene	15	2500	1.38

Table 2
Relative Benzene Retention Efficiencies
of Various Adsorbents

Adsorbent	Percent Absorbed at 30°C	Percent Absorbed at 0°C
Activated alumina	0	0
Silica gel	0	100
Activated charcoal	80	90
Molecular sieve	100	100

Table 2 refers to the relative retention efficiencies of various adsorbents towards benzene. The data for activated alumina, silica gel, and activated charcoal were computed from the results of Philip West et al. (9) and compared with molecular sieve on the same basis.

Type 13X molecular sieve will in many cases adsorb unsaturated or polar organic compounds at low adsorbate partial pressures to a higher equilibrium weight capacity than activated charcoal, silica gel, or activated alumina. For example, ethylene at 20 mm Hg partial pressure and 25°C is adsorbed by molecular sieve type 4A to approximately 6 wt-% at equilibrium, while charcoal's equilibrium capacity is only 2.5 wt-% and silica gel's about 1.75%. Acetylene (at 25°C and 20 mm Hg) is adsorbed by molecular sieve type 4A to 7 wt-%, by charcoal to 1.8 wt-%, and by silica gel to 1.5 wt-%. Molecular sieve at room temperatures adsorbs lower weight capacities of methane or ethane at low partial pressures (<20 mm Hg) than charcoal under the same conditions. However, in general, activated charcoal will have a much lower equilibrium capacity for organic compounds at low partial pressures than 13X molecular sieve, and its retention ability (Table 2) will also be inferior. (At high partial pressures activated charcoal's sorptive capacity is two to three times that of 13X sieve.)

Adiabatic Adsorption

The adsorption of water will raise the temperature of the effluent gas from a molecular sieve bed. Thus for an influent R.H. of 50% and flow of 2500 cm/minute at 25°C, the effluent temperature will reach approximately 95°C. This will adversely affect the coadsorption of organic vapors. For example, under the same conditions of flow, temperature, and R.H., the H_2O dew point of the effluent gas will rise from -98°C (approximate water concentration 0.02 ppm) to -70°C (2.5 ppm) when the adsorption is changed from isothermal to adiabatic (5). The minimum effluent concentration of the more volatile mononuclear aromatics, such as benzene and toluene, will not be as low as this. Therefore, if the concentration of the organic vapor effluent is to be at or below 1.0 ppm, the organic adsorption must be maintained isothermal (effluent temperature <40°C).

Reactivation

In general, a sufficiently hot (150°C) purge gas will remove low boiling nonpolar organic adsorbates from a bed containing only organic adsorbates. If temperature sensitive substances are present, it is necessary to displace the organic adsorbate with water vapor followed by removal of the adsorbed water (9). At room temperature, water will displace the adsorbed organic (Table 3) provided no chemical reaction such as polymerization or decomposition has taken place. (Freon 22 decomposes with evolution of CO_2 on 5A molecular sieve at room temperature (10).)

Table 3
Reactivation by Various Purge Gases

Influent	Duration (minutes)	Temperature (°C)	Flow Rate (cm/minute)	n-Decane Sorbed (wt-%)	Decane Displaced (%)
Air*	1200	20	2500	12.25	0
CO₂†	1440	20	550	14.50	8.69
CO₂	2480	20	550	14.50	21.64
Air	960	125	0	13.00	48.42
Air‡	72	20	2500	14.49	100.0

*Tube, 1.52 cm in diameter; bed height, 12 cm.
†Tube, 1.95 cm in diameter; bed height, 12 cm.
‡H_2O vapor pressure, 13.46 mm Hg.

Generally the higher boiling or more polar organics will displace the more volatile, less polar adsorbates. Decane, for example, will displace carbon dioxide.

The replacement of n-decane by H_2O occurs rapidly; in fact, water sorbs on the sieve at the same rate as it would on clean sieve material (Table 4). Water replaced benzene, toluene, xylene, pyridine, and aniline at room temperature, but heat in addition to water was required for complete removal of nitrobenzene (Table 5). It is concluded, therefore, that highly polar organic compounds would require heat together with H_2O (1,5) in order to remove all traces of the organic materials.

From closed system regeneration studies, it was found that coadsorbed water can be used in reactivating molecular sieve by simply heating and purging in the same direction as the gas flow during the adsorption cycle. The amount of sorbed water should be at least equal to the weight of the coadsorbed organic compounds. Adsorbed water will replace the organic adsorbate as it moves down the column. This procedure successfully regenerated sieves containing water and one of the following coadsorbed organic compounds, n-decane, benzene, toluene, pyridine, xylene, aniline, and nitrobenzene.

Table 4
H_2O Breakthrough Time of 13X Samples Coadsorbing
n-Decane Compared With
Breakthrough Time of Organic-Free Samples

Influent n-Decane (ppm)	Influent H_2O Vapor Pressure (mm Hg)	Weight-% H_2O at H_2O Breakthrough	H_2O Breakthrough (minutes/cm of sieve)	
			Decane Present	Decane Absent
0	10.94	17.08	-	3.98
50	11.52	17.25	3.81	3.79
128	8.33	16.90	4.85	5.16
590	8.33	16.85	4.84	5.16
300	5.47	17.30	8.26	8.08
1255	5.47	17.60	8.39	8.22

Table 5
Reactivation by Displacement With H_2O*

Adsorbate	Weight-% Sorbed	Weight-% H_2O After Displacement of Organic
H_2O	-	25.5
Benzene	10.85	27
Toluene	12.38	25.2
Xylene	13.26	25.0
Aniline	14.20	24.7
Nitrobenzene	2.04	18.96

*Sample weight, 12 grams; air flow, 550 cm/minute at 20°C and 95% R.H. for 16 hours. Desorption conditions for H_2O: dry nitrogen purge at 550 cm/minute and maximum temperature of 260°C. The weight-percent of organic absorbate remaining after H_2O desorption was zero for all absorbates listed.

The conditions of temperature and flow required for reactivation of moist sieve can be seen in Table 6. Table 7 summarizes the various purge gas temperatures required for complete regeneration at different purge gas dew points.

EXPERIMENTAL ERROR

The chief sources of error are: Burette readings, organic vapor dew point measurements, and the capillary-T-connector procedure.

The Burette Error

The volume of liquid at breakthrough for an average sieve sample of 12 grams was 1.70 ml (n-decane). The reading error was about 1-1/2 mm, corresponding to 0.01 ml. Thus the probable error for this system was ±0.6%.

Organic Vapor Dew Point Measurement

Dew points at the -60°C range could be repeated within one degree. This resulted in a possible error in the influent concentration of ±4%.

Capillary T-Connector Procedure

The accuracy in determining 50-mg increments of adsorption by weighing the sample tube, trap, and adsorbate bottle was ±2 mg; the corresponding error was ±4%.

Table 6
Reactivation of H_2O Saturated 13X Samples at 1 Atmosphere
and Various Flow Rates*

Temperature (°C)	Linear Flow (cm/minute)	Grams H_2O	Weight-% H_2O	Time Required (minutes)	Percent Reactivated
125	200	9.5	23.46	1350	56.84
125	204	10.7	23.05	1330	85.05
125	612	10.8	23.27	210	81.60
125	1224	10.7	23.00	125 450	82.20 93.20
125	4082	11.0	23.70	268	86.40
205	102	11.2	23.28	190	94.64
205	407	11.9	24.71	285	100
205	1152	12.0	24.95	160	100
252	102	12.3	25.60	30	100
252	408	12.3	25.57	24	100
305	102	14.50	25.44	12	100

*Bed height, 15 cm: bed diameter, 2.5 cm. Average sample weight of
active sieve material 45 grams.

Table 7
Required Temperature for Complete
Regeneration at a Given Purge Gas Dew Point*

Purge Gas Dew Point (H_2O Dew Point)	Temperature (°C)
-40	343
-48	315
-57	260
-68	204

*Taken from Linde molecular sieve data sheets.

SUMMARY

A 13X molecular sieve adsorption system for organic compounds has the following advantages over other adsorbent methods:

1. It furnishes a high degree of air purification at fast flow rates and low influent concentrations.

2. For concentrations in a ppm range, it has high equilibrium capacities for most organic vapors when compared with charcoal, silica gel, and alumina.

3. It has low pressure drops in comparison with adsorbent charcoal of the same size.

4. Molecular sieve has a high degree of thermal stability.

5. It shows long service life and consistent performance.

Its disadvantages are:

1. A high temperature is required for regeneration to the sieve when water is present.

2. If removal of organic vapor contaminants to level below 5 ppm is desired, adsorption conditions must be isothermal.

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